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Organometallic Chemistry of High-Valent Ni(III) and Ni(IV) Complexes

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10.1 Introduction

Nickel (Ni) is commonly used as a catalyst for various cross-coupling reactions, including Negishi, Kumada, and Suzuki couplings. Although the 0, I, and II oxidation states of Ni are commonly involved in these catalytic transformations, recent studies show that the III and IV oxidation states of Ni also play a key role in organic transformations such as C–C and C–heteroatom bond formation reactions.

The first organometallic Ni^{III} and Ni^{IV} complexes were reported almost 40 years ago, when they were observed by Kochi in 1978 and Smart in 1982, respectively. However, it is only in the past decade that many advances have been made in the synthesis of high-valent organometallic Ni complexes as also the detailed study of their reactivity and involvement in various organic transformations. The once elusive Ni^{III} and Ni^{IV} species are now promoting a wide range of organic transformations in a complementary manner to the reactions involving Ni⁰ and Ni^{II} intermediates.

In this chapter, we will present accomplishments made in the past 40 years involving organometallic Ni^{III} and Ni^{IV} complexes, with a focus on the more recent systems that exhibit rich reactivity profiles. It is important to note that there are other high-valent, non-organometallic Ni complexes that provide key insight into the role of various Ni intermediates in organic transformations, and such species are also presented herein.

10.2 Organometallic Ni(III) Complexes

Kochi and coworker published in 1978 the first organometallic Ni^{III} species, **1** (Figure 10.1), that was observed by EPR and UV–Vis spectroscopy. Oxidation of the Ni^{II} precursor with sodium hexachloroiridate at –50 °C yielded an EPR-active

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Figure 10.1 The first observed organometallic Ni^{III} species by Kochi and coworkers in 1978.

species with an absorption maximum at 410 nm, suggestive of a Ni^{III} intermediate. Warming up of the solution led to the disappearance of EPR signal, which was associated with a reductive elimination from the Ni^{III} species [1].

It was not until 1983 that van Koten and coworkers isolated the first high-valent nickel organometallic complex using the pincer ligand 1,1'-(1,3-phenylene) bis(*N,N*-dimethylmethanamine) (NCN, Figure 10.2). The binding of the tridentate NCN pincer ligand and two anionic ligands yielded stable trigonal bipyramidal Ni^{III} complexes **2**. The auxiliary ligands in the *cis* coordination sites could easily be exchanged with nitrite or nitrate to generate **3**, or with isothiocyanate and pyridine to yield **4** and **5**. All these complexes are unusually stable and have only been proposed as intermediates in the Kharasch radical addition of CCl₄ to alkenes [2–6].

In 2018 Zargarian and Cloutier revisited the reactivity of complexes **2** and were able to show that they undergo C–X bond formation at the *ipso* C atom of the

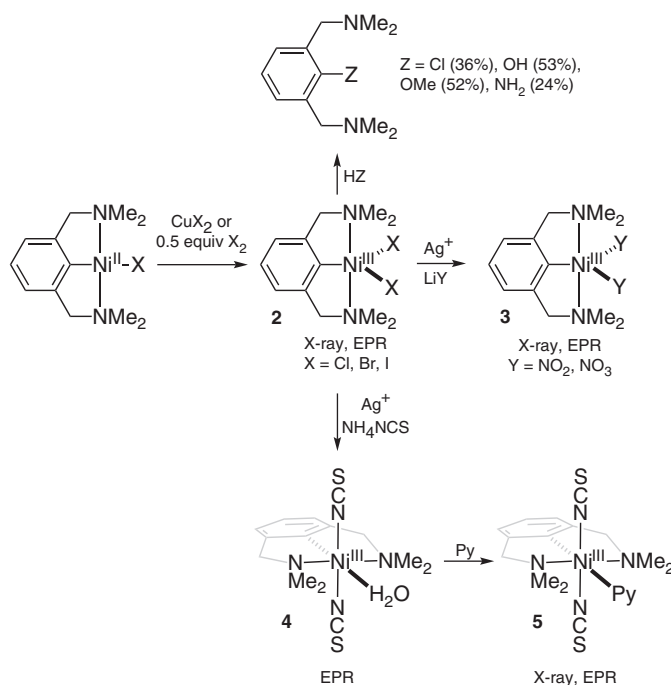


Figure 10.2 The first isolated organometallic Ni^{III} complexes stabilized by an NCN pincer ligand reported by van Koten and coworkers, and their subsequent reactivity reported recently by Zargarian and coworkers.

phenyl group with water, alcohols, amines, and strong acids under mild conditions [7].

In 1995, van Koten and coworkers introduced a chiral pincer ligand containing amino-acid-derived arms. In contrast to their original NCN ligand, this histidine-type NCN pincer ligand could coordinate to the Ni center either in a tridentate or a pentadentate manner. In this case, the Ni^{III} complex **6** adopts an octahedral geometry and can be isolated in 72% yield (Figure 10.3) [8].

In 1995, Hillhouse and coworkers suggested the formation of a Ni^{III} intermediate after exposing the Ni^{II} precursor to either O₂ or I₂ at room temperature (Figure 10.4). The reactions resulted in clean formation of *N-p*-tolylpyrrolidine, while the one-electron oxidant acetylferrocenium tetrafluoroborate also cleanly converts the Ni^{II} to **7**, supporting the formation of the transient Ni^{III} species [9, 10].

In addition, the same authors reported the reactivity of the dimeric seven-membered nickel(II) oxametallacycle, which in presence of O₂ leads to the formation of a new C—O bond (Figure 10.5). An oxidatively induced mechanism was proposed that involves the formation of a transient Ni^{III} intermediate, **8**, followed by reductive elimination to give 4,4-dimethylchroman [10, 11].

Figure 10.3 The first isolated chiral Ni^{III} organometallic complex stabilized by an amino acid pincer ligand.

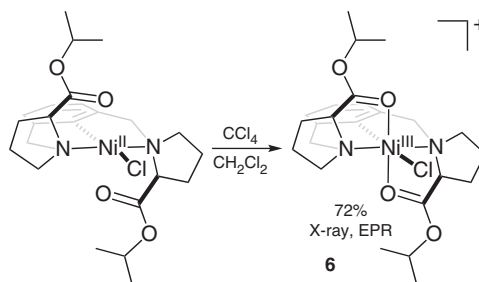


Figure 10.4 Oxidatively induced C—N bond formation from a Ni^{II} complex through a transient Ni^{III} species.

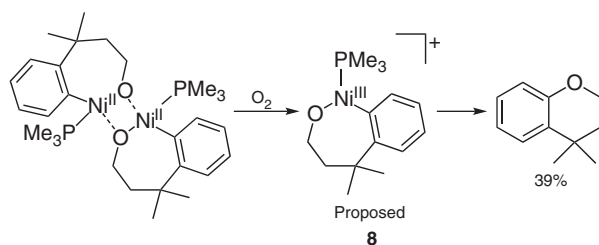
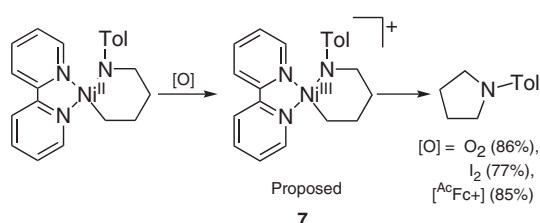


Figure 10.5 Oxidatively induced reactivity of a dimeric seven-membered Ni^{II} oxametallacycle.

In 2002, Hillhouse and coworkers described the stereochemical synthesis of aziridine by an oxidatively induced reductive elimination (Figure 10.6). Reaction of *N*-tosylaziridine with (bpy)Ni⁰(COD) gives only one regioisomer of the azametallacyclobutane complex, the oxidative addition occurring exclusively at the least hindered C–N bond. Addition of O₂ generates a proposed Ni^{III} intermediate **9**, which undergoes reductive elimination with inversion of stereochemistry to reform the aziridine with 92% inversion, as observed by ¹H NMR [12].

In 2005, Warren and coworkers isolated a trigonal planar Ni^{III} complex, **10**, stabilized by a bidentate β-diketiminato ligand and an imidoadamantane group (Figure 10.7). The reactivity of the terminal imido group with CO, ^tBuNC, and PMe₃ result in the formation of OC=N, NC=N, and P=N bonds, respectively [13].

Starting in 2007, Zargarian and coworkers have employed the 1,3-bis((diisopropylphosphaneyl)oxy)propane (PCP) and 1-(3-((diisopropylphosphaneyl)oxy)phenyl)-*N,N*-diN^Rmethanamine (PCN) phosphonite pincer ligands to stabilize Ni^{III} complexes **11** and **12**, respectively (Figure 10.8). Similar to the (NCN)Ni complexes reported by van Koten and coworkers, the PCP/PCN-supported Ni^{III} species could promote radical Kharasch addition of CCl₄ to alkenes in good yields [14–16].

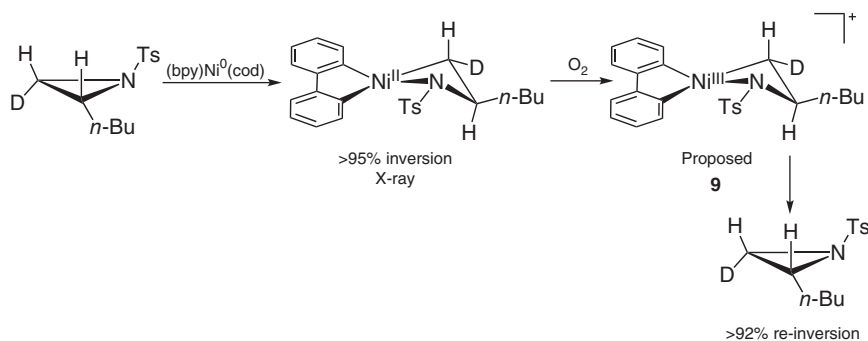


Figure 10.6 The formation of aziridine by an oxidatively induced reductive elimination from Ni^{III}.

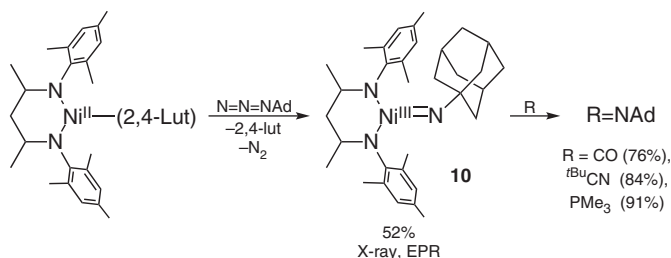


Figure 10.7 Reactivity of a trigonal planar Ni^{III}-imido complex to give N–X bond formation products.

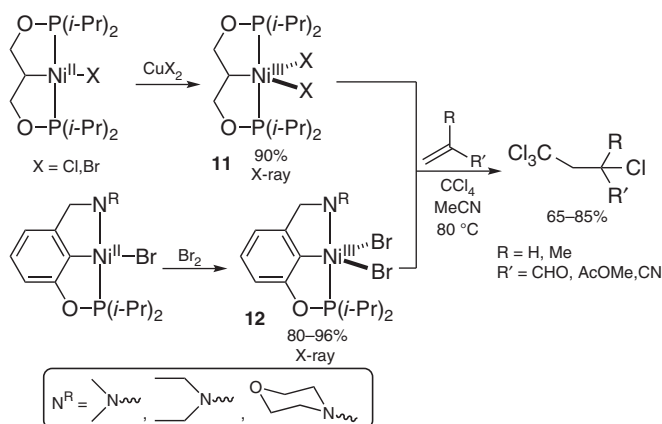


Figure 10.8 Ni^{III} complexes supported by phosphonite pincer ligands isolated by Zargarian and coworkers, and their radical Kharasch addition reactivity.

In 2008, Zargarian and coworkers used the PCP pincer ligand 1,5-bis(diisopropylphosphanyl)pentyl to stabilize a Ni^{III} complex **13** with a trigonal bipyramidal geometry (Figure 10.9). In contrast to the complexes supported by the PCP phosphonite ligands, **13** does not exhibit significant reactivity at the Ni^{III} center [17].

Hillhouse and coworkers synthesized in 2011 two Ni^{III}-imido complexes supported by 1,2-bis(di-*tert*-butylphosphino)ethane (Figure 10.10). The oxidation of the Ni^{II} complexes led to the formation

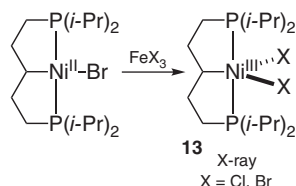


Figure 10.9 Aliphatic PCP-Ni^{III} complexes isolated by Zargarian and coworkers in 2008.

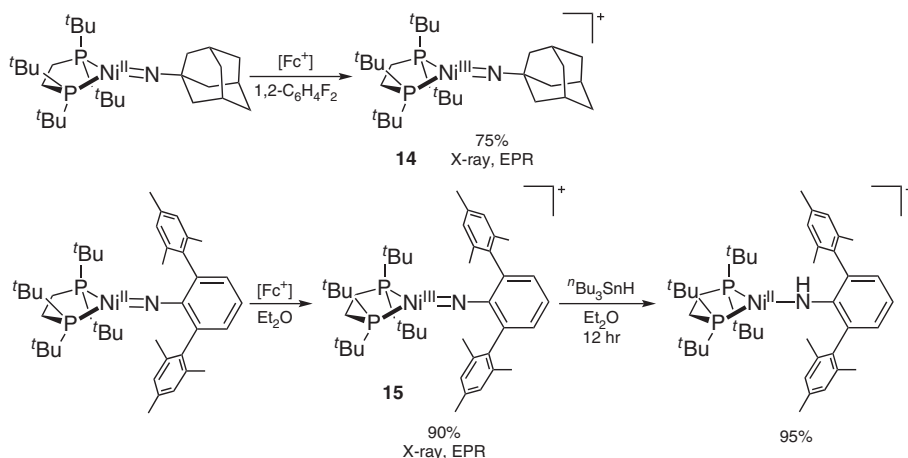


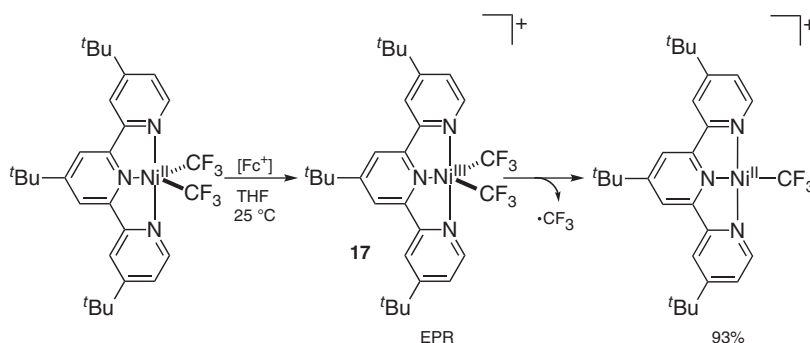
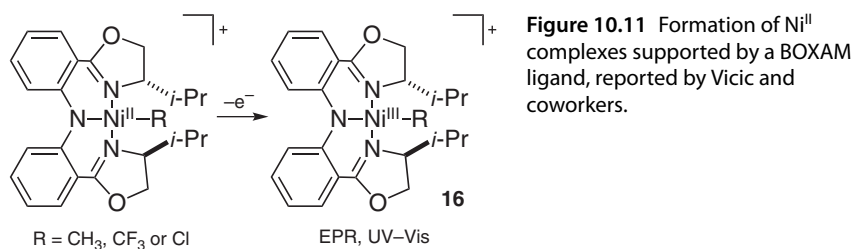
Figure 10.10 Isolated Ni^{III} alkyl/aryl-amido complexes reported by Hillhouse and coworkers in 2011.

of two Ni^{III} aryl/alkyl-imido complexes. Both Ni^{III} species exhibit analogous EPR spectra at low temperature, yet different variable-temperature magnetic properties and a low-spin/high-spin equilibrium was proposed to take place for the alkylimido Ni^{III} complex **14** to account for the difference. The Ni^{III}-arylimido complex **15** can undergo hydrogen atom abstraction when reacted with ⁿBu₃SnH to generate a Ni^{II}-amide complex [18].

Vicic and coworkers reported in 2012 the one-electron oxidation of Ni^{II} complexes supported by the BOXAM ligand (BOXAM = bis((4-isopropyl-4,5-dihydrooxazol-2-yl)phenyl)amine (Figure 10.11). The resulting Ni^{III} complexes **16** were characterized by EPR and UV–Vis spectroscopy, and it was shown that their redox behavior strongly depends on the co-ligand (CH₃, CF₃, or Cl) [19, 20].

In addition, in 2013 Vicic and coworkers reported a five-coordinate Ni^{III} complex supported by a terpyridine ligand and two fluoroalkyl ligands (Figure 10.12). Ferrocenium hexafluorophosphate was used to oxidize the Ni^{II} complex to a transient Ni^{III} species **17**, which undergoes elimination of one CF₃ group, likely through a reductive homolysis of a trifluoromethyl radical [21].

In 2013, Tilley and coworkers reported an isolable Ni^{III}-alkyl complex, **18**, which has been prepared through a two-electron oxidative addition of MeI to a Ni^I complex (Figure 10.13). Complex **18** is thermally unstable and decomposes in one day in benzene to give ethane and a Ni^{II} complex [22, 23]. Interestingly, the bis-amido ligand framework is capable of supporting Ni complexes in three different oxidation states.



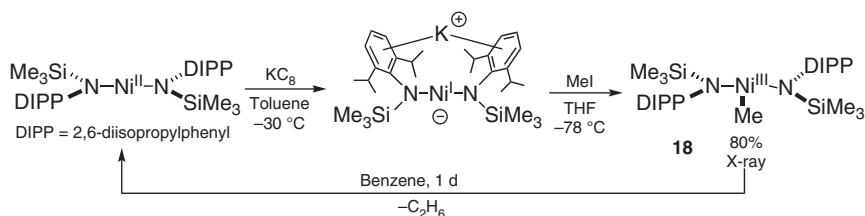


Figure 10.13 Synthesis of a Ni^{III}-alkyl species formed upon oxidative addition of MeI to a Ni^{II} precursor.

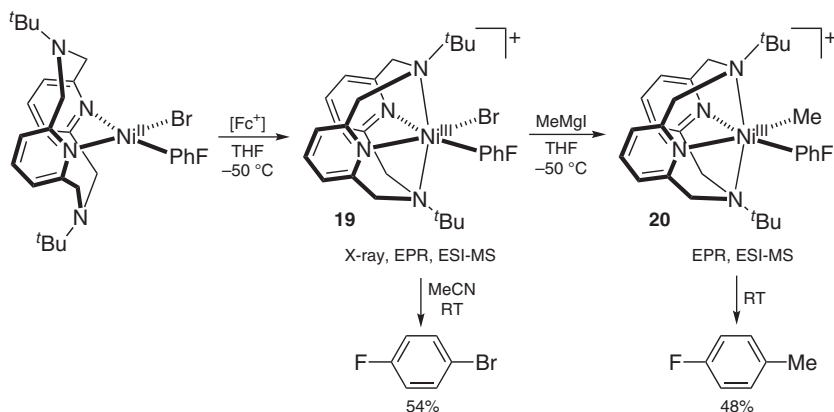
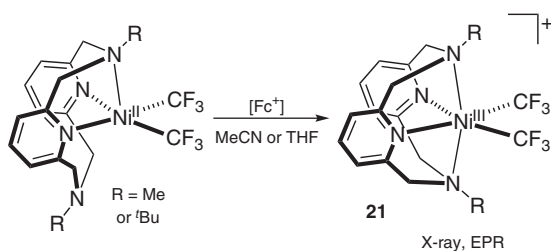


Figure 10.14 Synthesis and reactivity of Ni^{III}(aryl)halide and Ni^{III}(aryl)alkyl complexes reported by Mirica and coworkers in 2014.

Mirica and coworkers published in 2014 a series of Ni^{III}(aryl)halide complexes stabilized by the tetradentate ligand *N,N'*-di-*tert*-butyl-2,11-diaza[3,3](2,6)pyridophane (Figure 10.14). The Ni^{III}(aryl)halide complex **19** is stable at low temperature, yet undergoes rapid C–halide bond formation at room temperature. The Ni^{III}(aryl)halide complex also undergoes a rapid transmetalation reaction with Grignard reagents to yield a detectable Ni^{III}(aryl)alkyl complex **20**, followed by rapid C–C bond formation at RT [24].

In addition, Mirica and coworkers published in 2015 the synthesis of stable organometallic Ni^{III} complexes that contain two trifluoromethyl ligands and are supported by tetradentate N-donor ligands ^RN₄ (R = Me or *t*Bu, Figure 10.15). Interestingly, the corresponding Ni^{II} precursors undergo facile oxidation,

Figure 10.15 Synthesis of stable bis(trifluoromethyl)nickel^{III} complexes supported by tetradentate pyridinophane ligands.



including aerobic oxidation to generate the Ni^{III} complexes **21**. Unlike most other organometallic Ni^{III} complexes, complexes **21** are indefinitely stable at RT under N₂, while heating at 80 °C for 24 hours or photolysis with visible light at RT produces only trace amounts of CF₃H and C₂F₆ [25].

Mirica and coworkers reported in 2015 the synthesis of several Ni^{III} complexes supported by a modified tetradentate pyridinophane ligand containing one phenyl group (Figure 10.16). The Ni^{III}(MeCN)Br complex **22** was generated by one-electron oxidation of the Ni^{II} precursor, while halogen abstraction with silver gives a Ni^{III}-disolvento complex **23**, which is an RT-stable dicationic complex. Interestingly, the Ni^{III}-dimethoxy complex **24** undergoes aryl methoxylation that is favored by addition of the PhI(PyOMe)₂OTf₂ oxidant-suggesting the formation of a Ni^{IV} intermediate, followed by rapid reductive elimination to generate the C—O bond formation product [26].

In 2015, Vicic and coworkers reported the isolation of a [(tpy)Ni^{III}(C₄F₈)]⁺ complex **25** (tpy = terpyridine) stabilized by the cycloperfluorobutyl -C₄F₈- ligand (Figure 10.17). The Ni center in **25** adopts a distorted octahedral geometry,

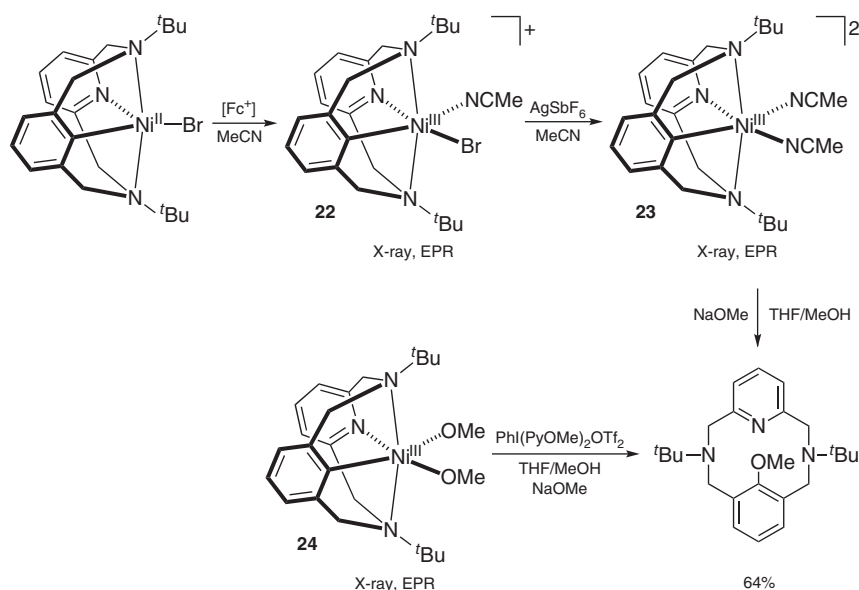


Figure 10.16 Synthesis of Ni^{III} complexes supported by a modified pyridinophane ligand containing one phenyl group.

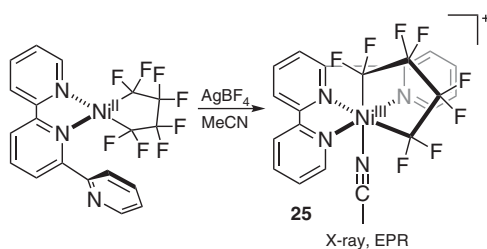


Figure 10.17 Formation of a stable (tpy)Ni^{III}(C₄F₈) complex reported by Vicic and coworkers in 2015.

where Ni—N bonds *trans* to the fluoroalkyl ligand were shorter by about 0.2 Å than the Ni—N bonds that are *cis* to the fluoroalkyl groups [27].

In 2016, Diao and coworkers proposed a square pyramidal Ni^{III}-alkyl complex **26** stabilized by the bidentate anionic ligand 3,5-dimethyl-2-(2-pyridyl)pyrrole (Figure 10.18). This unstable intermediate is thought to form an iodide-bridged Ni^{III} dinuclear complex **27**, which undergoes rapid reductive elimination to form ethane in 43% yield [28].

In addition, a mixed-valent Ni^{II}/Ni^{III} dinuclear complex **28** stabilized by four triazabicyclodecene (TBD) ligands was reported by the same group (Figure 10.19). Attempts to oxidize **28** with 1.5 equiv PhICl₂ did not lead to the isolation of the di-Ni^{III} complex **29**; instead, the N—N coupling of two TBD ligands was observed [29].

In 2016, Mirica and coworkers reported a series of Ni^{III} complexes **30** and **31** that undergo aromatic cyanoalkylation (Figure 10.20). Addition of base to the Ni^{III}(MeCN)₂ complex **31** gives the cyanomethylated product in quantitative yield. Regioselective α-cyanoalkylation was also observed with various nitrile substrates to generate secondary and tertiary nitriles [30].

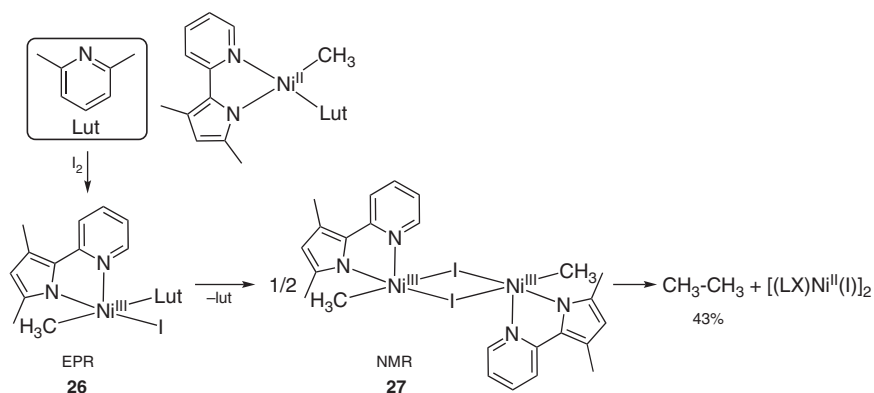


Figure 10.18 Synthesis of mono- and dinuclear square pyramidal Ni^{III}-alkyl complexes.

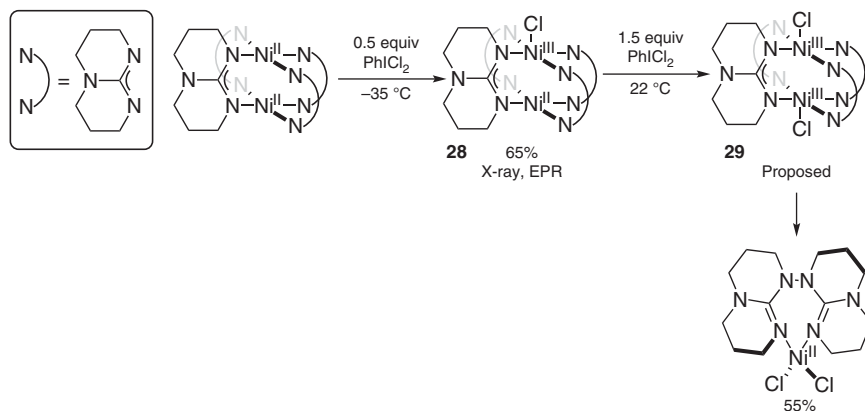


Figure 10.19 N—N bond formation from a Ni^{III} dimer published by Diao and coworkers in 2016.

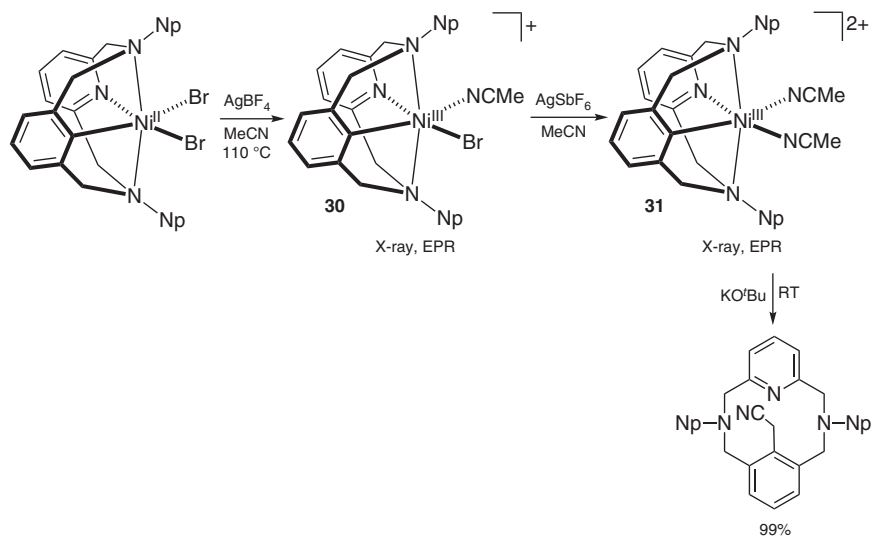


Figure 10.20 Synthesis of Ni^{III} complexes and their aromatic cyanoalkylation reactivity.

In 2016, Mirica and coworkers synthesized the first isolated Ni^{III}-dialkyl complex, stabilized by the *N,N'*-dimethyl-2,11-diaz[3.3](2,6)pyridinophane ligand (Figure 10.21). The Ni^{III} complex **32** was shown to generate ethane in 54% yield over 24 hours at RT. However, the addition of 1 equiv of oxidant to the Ni^{III} complex **32** led to clean formation of ethane in 84% yield, while addition of 2 equiv of oxidant to the Ni^{II} precursor generated an almost quantitative amount of ethane within 30 minutes at RT. These results suggest that access to a Ni^{IV} intermediate should lead to fast reductive elimination and C—C bond formation [31].

In 2016, Company and coworkers observed a Ni^{III}-OCl intermediate stabilized by a tetradentate macrocyclic ligand (Figure 10.22). Oxidation of the Ni^{II} complex with 3 equiv Ca(OCl)₂ leads to the formation of a square pyramidal complex

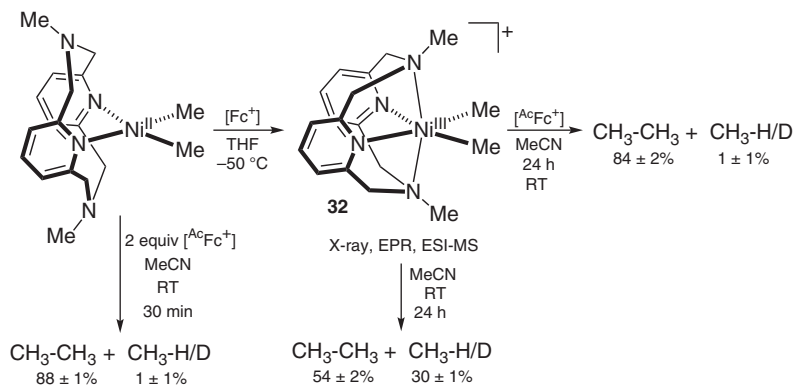


Figure 10.21 Synthesis and reactivity of the Ni^{III}-dialkyl complex reported by Mirica and coworkers in 2016.

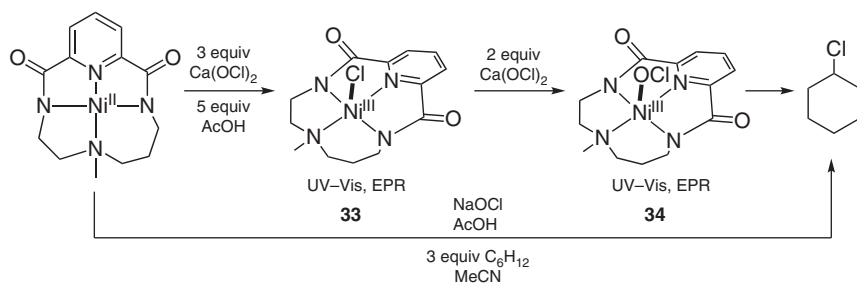


Figure 10.22 Catalytic oxidation of cyclohexane through a Ni^{III}-OCl intermediate.

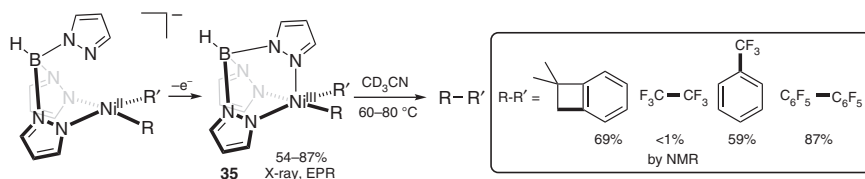


Figure 10.23 C—C bond formation from isolated organometallic Ni^{III} complexes stabilized by a trispyrazolylborate ligand.

33. However, addition of 2 equiv more of $\text{Ca}(\text{OCl})_2$ leads to the formation of the Ni^{III}-perchlorate complex **34**, which is thought to be the active intermediate in the catalytic oxidation of cyclohexane [32].

In 2016, Sanford and coworkers isolated a series of Ni^{III} complexes **35**, stabilized by an anionic trispyrazolylborate ligand and different C(sp²), C(sp³), and CF₃ ligands (Figure 10.23). Upon heating at mild temperatures, these complexes undergo reductive elimination of the organic ligands to generate the corresponding C—C bond formation products [33].

In 2017, Diao and coworkers observed the formation of dinuclear Ni^{III} complexes **36** and **37** stabilized by benzoquinoline and carboxylate ligands (Figure 10.24). While complex **36** undergoes reductive elimination to generate

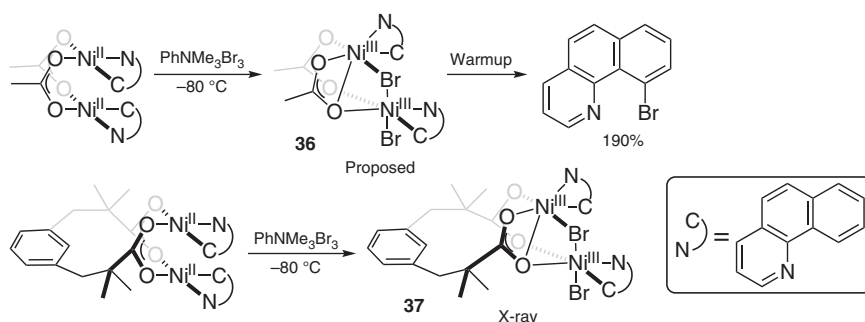


Figure 10.24 C—Br bond formation from a dinuclear Ni^{III} complex supported by benzoquinoline and carboxylate ligands.

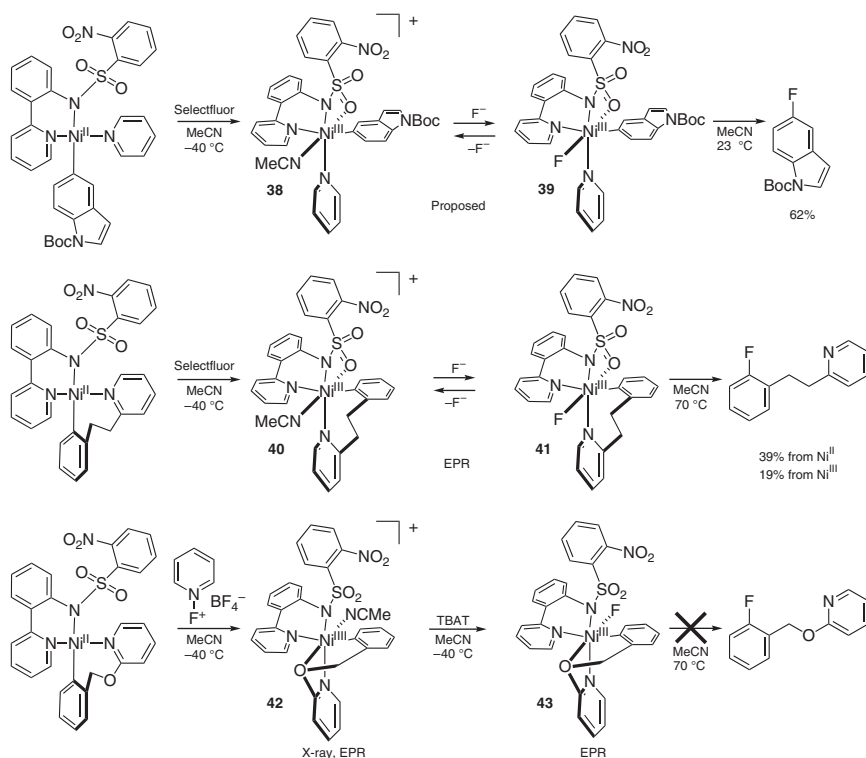


Figure 10.25 C—F bond formation from well-defined Ni^{III}(aryl)fluoride complexes reported by Ritter and coworkers in 2017.

10-bromobenzoquinoline, the structurally characterized complex **37** is stable and does not lead to C—Br bond formation [34].

In 2017, Ritter and coworkers reported C—F bond formation from well-defined Ni^{III}(aryl)fluorides complexes stabilized by the bidentate ligand 2-(2-pyridinyl)phenyl-2-nitrobenzenesulfonamide (Figure 10.25). These Ni^{III} species were generated by addition of Selectfluor to the Ni^{II} precursors. While complexes **38** and **39** could not be isolated since they rapidly generate the C—F bond formation product, complexes **40** and **41** could be detected by EPR prior to the reductive elimination step. By contrast, an isolable Ni^{III} complex **42** could be generated when an aryl ligand containing an O atom was employed. Although the Ni^{III}-F complex **43** was also detected by EPR, no C—F bond formation was detected in this case [35].

10.3 Organometallic Ni(IV) Complexes

In 2003, Dimitrov and Linden reported a quasi-tetrahedral Ni^{IV} complex **44** stabilized by four anionic ligands (three 1-norbornyl ligands and a halide ion) generated upon oxidation of a nickelate precursor with O₂ at -60°C

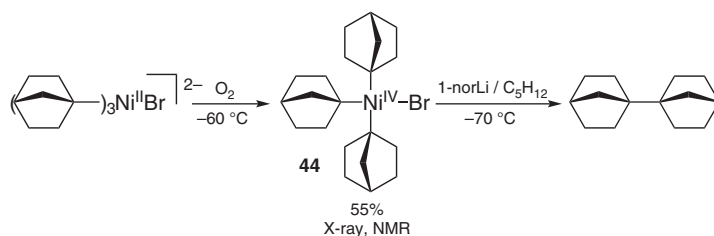


Figure 10.26 Formation of a quasi-tetrahedral Ni^{IV} complex and its C—C bond formation reactivity published by Dimitrov and coworkers in 2003.

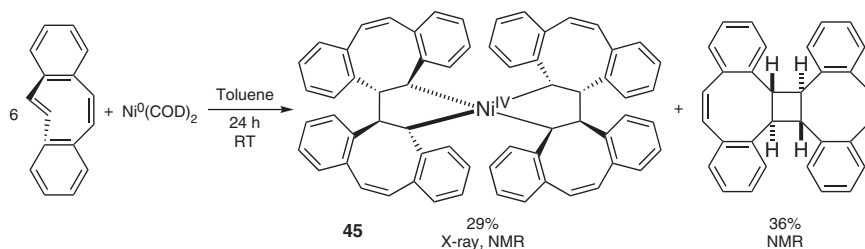


Figure 10.27 Synthesis of a stable tetraalkyl Ni^{IV} complex published by Nuckols and coworkers.

(Figure 10.26). Addition of 1 equiv of 1-norbornyl lithium to **44** in an attempt to remove the halide ligand and isolate a homoleptic Ni^{IV} complex was unsuccessful; instead, the C—C bond formation product di-norbornene was observed [36].

Nuckols and coworkers reported in 2009 a stable tetraalkyl Ni^{IV} complex **45** stabilized by two (5*Z*,11*E*)-dibenzo[*a,e*]cyclooctatetraene ligands (Figure 10.27). Interestingly, this Ni^{IV} complex is air-stable and can be heated to above 290 °C before any decomposition is observed, although during its synthesis a C—C bond formation product is obtained [37].

It is important to mention that starting in 2013, Chatani and coworkers reported Ni-catalyzed alkylation and arylation reactions involving C—H bond activation of benzamides and acrylamides. The proposed mechanisms involve a C—H bond activation via a concerted metalation–deprotonation step at a Ni^{II} species **46** to generate **47** (Figure 10.28), followed by oxidative addition of butyl bromide to generate a Ni^{IV} intermediate **48**. Subsequent reductive elimination to form **49** followed by protonation yields the alkylation product and regenerates the Ni^{II} precursor [38, 39].

In 2015, Sanford and Camasso isolated an octahedral Ni^{IV} complex **50** stabilized by a neutral scorpionate tris(2-pyridyl)methane ligand, a cyclic alkyl/aryl C-donor ligand (—CH₂CMe₂-*o*-C₆H₄—), and a trifluoromethyl group (Figure 10.29). Upon heating **50** at 95 °C for seven hours, the C—C bond formation benzocyclobutane product was obtained in quantitative yield, while addition of acetate generates the C(sp³)—O bond formation product at RT [40].

Similarly, the anionic trispyrazolylborate ligand stabilizes a Ni^{IV} complex **51**, which does not undergo reductive elimination of benzocyclobutane. Addition

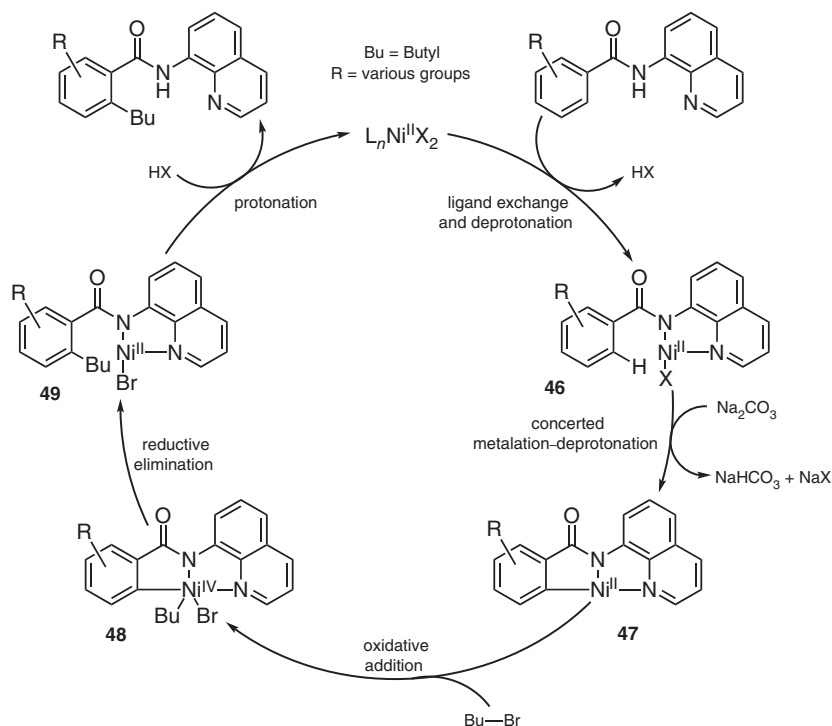


Figure 10.28 Proposed nickel-catalyzed alkylation mechanism involving Ni^{IV} intermediates by Chatani and coworkers.

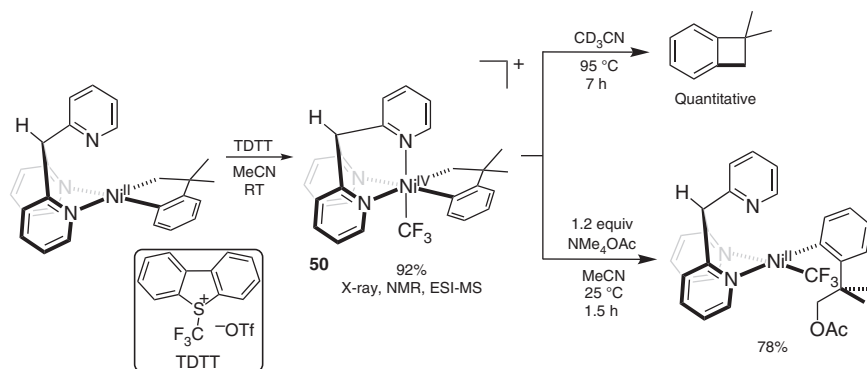


Figure 10.29 An isolated [tris(2-pyridyl)methane]Ni^{IV}(cyclonephyl)(CF₃) complex and its C(sp²)—C(sp³) and C(sp³)—OAc bond formation reactivity.

of different nucleophiles results in quantitative formation of the corresponding C(sp³)—X bond formation product (Figure 10.30), while addition of azide results in the formation of indoline in quantitative yields [40]. In addition, other Ni^{III} and Ni^{IV} complexes supported by the trispyrazolylborate ligand and various axial ligands were reported in 2017 [41].

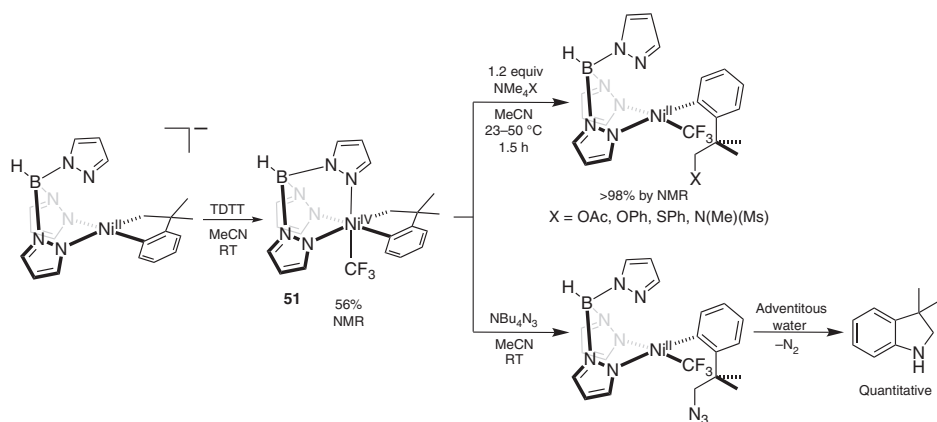


Figure 10.30 An isolated (trispyrazolylborate)Ni^{IV}(cycloneophyl)(CF₃) complex and its C(sp³)—X bond formation reactivity.

In 2015, Sanford and coworkers reported the synthesis of various (trispyrazolylborate)Ni^{IV}(aryl)(CF₃)₂ complexes **52** using either a trifluoromethylating agent or aryl electrophiles (Figure 10.31). Upon heating, these complexes undergo trifluoromethylation of the Ni-aryl group, the electron-donating aryl group undergoing reductive elimination more rapidly [42].

In 2016, Fout and coworkers isolated an octahedral Ni^{IV} complex **53** supported by an anionic, tridentate bis(diisopropylphenyl-benzimidazol-2-ylidene)phenyl ligand and three bromide ligands (Figure 10.32). Complex **53** acts as a bromide transfer reagent for the bromination of different organic substrates including styrene, cyclohexene, mesitylmagnesium bromide, and lithium hexamethyldisilazide [43].

In 2017, Sanford and coworkers probed the intramolecular C—H bond activation at a Ni^{IV} center by using the bis(2-pyridyl)(2-^Rphenyl)-fluoromethane ligand as a model system. Oxidation of the Ni^{II} complex under mild conditions results in C_{ipso}-H activation of the aryl ring on the ligand (Figure 10.33), and a range of (bis(2-pyridyl)(2-^Rphenyl)-fluoromethane)Ni^{IV}F(CF₃)₂ octahedral complexes **54** were isolated in good yields [44].

Mirica and coworkers reported in 2017 the synthesis of organometallic Ni^{III} and Ni^{IV} complexes **55** and **56** supported by a triazacyclononane ligand (Me₃tacn) and a cyclic C-donor ligand (–CH₂CMe₂-*o*-C₆H₄–, Figure 10.34). Interestingly, the five-coordinate Ni^{III} complex **55** is quite stable, and only

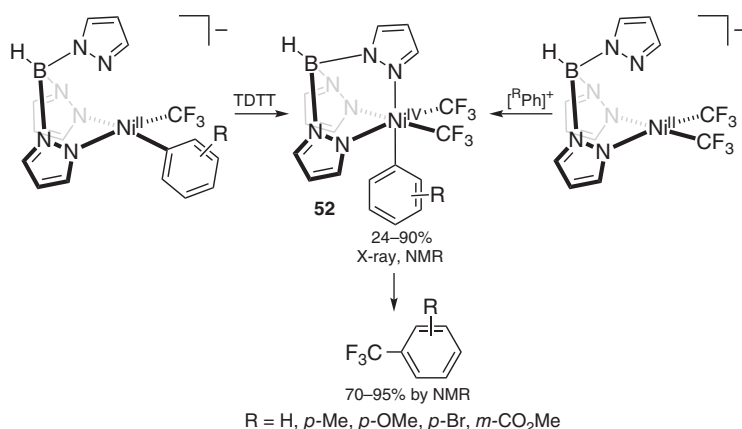


Figure 10.31 Isolated (trispyrazolylborate)Ni^{IV}(aryl)(CF₃)₂ complexes and their trifluoromethylation reactivity.

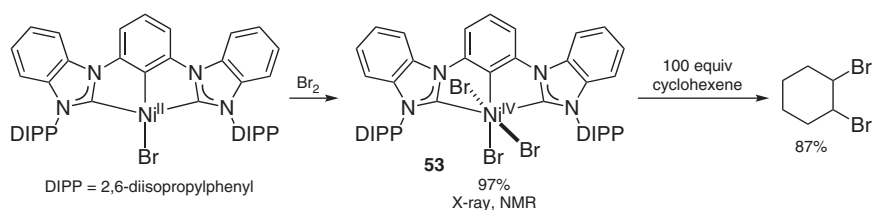


Figure 10.32 Bromination of alkenes using an isolated Ni^{IV}-tribromide complex.

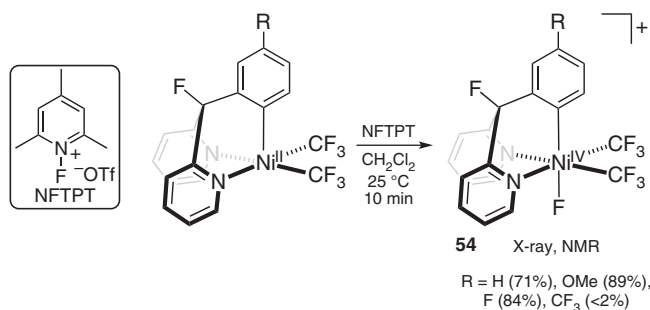


Figure 10.33 Oxidatively induced C–H activation of bis(2-pyridyl)(2-^R-phenyl)-fluoromethane Ni-aryl(CF₃)₂ complexes.

gives the C–C bond formation product in moderate yields upon heating. By contrast, exposure of the Ni^{IV} complex **56** to blue LED light leads to rapid and quantitative C–C bond formation. When heated in the presence of chloride, the Ni^{IV} complex **56** generates both C(sp²)–X and C(sp³)–X bond formation products [45].

In 2017, Nebra and coworkers reported the isolation of a stable octahedral Ni^{IV} complex **57** supported by the monodentate ligands pyridine, trifluoromethyl, and fluoride, along with mononuclear and dinuclear Ni^{III} complexes **58** and **59** (Figure 10.35). These complexes were generated by the addition of different amounts of XeF₂ to the same (py)₂Ni^{III}(CF₃)₂ precursor. Interestingly, the Ni^{IV} complex **57** promotes the trifluoromethylation of 1,2-dichlorobenzene in quantitative yields [46].

10.4 Other High-Valent Ni Complexes

10.4.1 Additional Ni^{III} Complexes

Included here are several other Ni^{III} complexes that have been isolated, yet they exhibit limited reactivity (Figure 10.36). In 1982, Smart and coworkers isolated the Ni^{III} complex **60** upon the one-electron oxidation of decamethylnickelocene [47, 48]. Starting in 2006, Liaw and coworkers isolated a Ni^{III} species **6**, supported by a trianionic, tetradentate triphenylphosphine-type ligand with thiolate arms [49, 50]. Using the same ligand framework, in 2010 Lee and coworkers isolated the first Ni^{III}-alkyl complexes **61** [51]. One year later, Kinoshita and coworkers obtained a halide-bridged Ni^{III} dinuclear complex **62** supported by the tetradentate ligand tris(2-pyridylthio)methanide [52]. Complex **62** slowly converts into the mononuclear Ni^{III} complex **63**, during which the ligand isomerizes to bis(2-pyridylthio)(2-thiopyridinium)methyl [52]. In 2012, Ray and coworkers observed a trigonal bipyramidal high-valent Ni^{III}-oxo complex **64** stabilized by the tetradentate tris[2-(*N*-tetramethylguanidyl)ethyl]amine ligand [53]. In the same year, Patra and coworkers observed a high-valent Ni^{III} species **65** supported by two tridentate *N*-2-methylthiophenyl-2'-pyridinecarboxamide ligands [54].

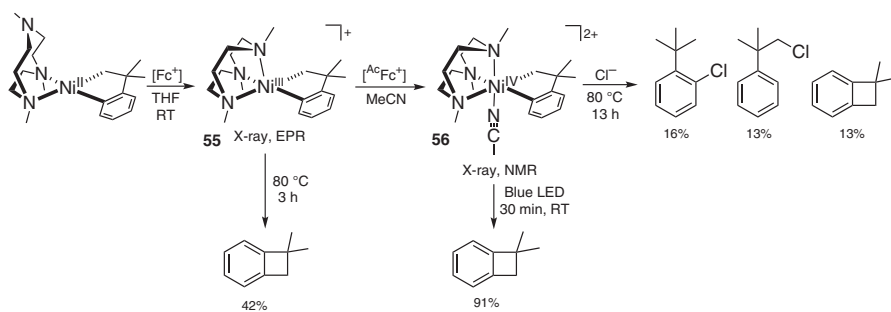


Figure 10.34 Synthesis of $(Me_3tacn)Ni^{III/IV}(CH_2CMe_2-o-C_6H_4)$ complexes and their C—C and C—Cl bond formation reactivity.

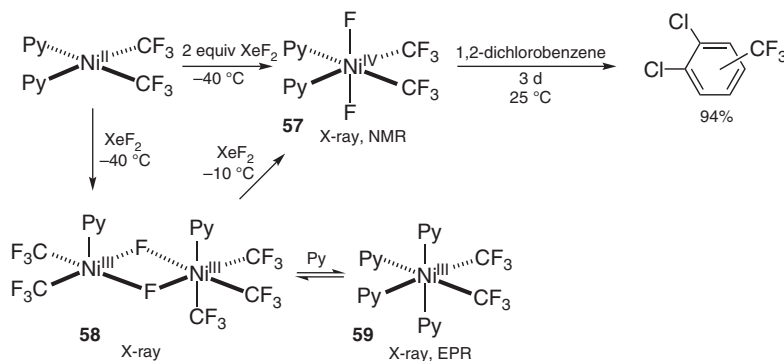


Figure 10.35 Trifluoromethylation of 1,2-dichlorobenzene using an isolated Ni^{IV} complex supported by pyridine.

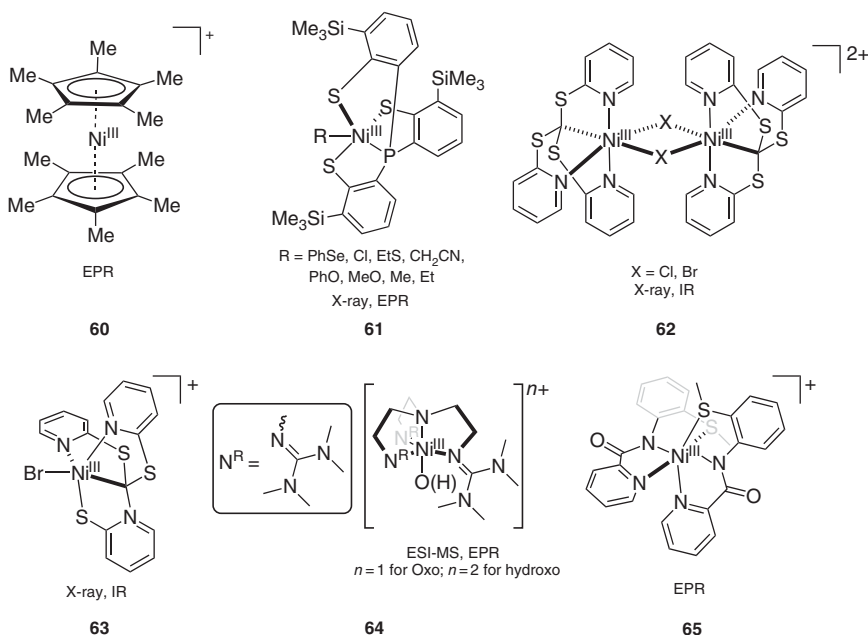


Figure 10.36 Additional isolated Ni^{III} complexes.

10.4.2 Additional Ni^{IV} Complexes

Included here are several other Ni^{IV} complexes that have been isolated, yet they exhibit limited reactivity (Figure 10.37). In 1982, the Ni^{IV} complex **66** was observed by Smart and coworkers upon oxidation by two electrons of the decamethylnickelocene Ni^{II} precursor [47, 48]. In 1994, Klein and coworkers published the first organometallic Ni^{IV} complex, **67**, which is stabilized by a chelating acylphenolato dianion, two trimethylphosphine ligands, and an iodide and methyl group [55, 56]. Another similar Ni^{IV} complex, **68**, which also adopts an octahedral geometry was reported a few years later [57]. In 1995, Gould and

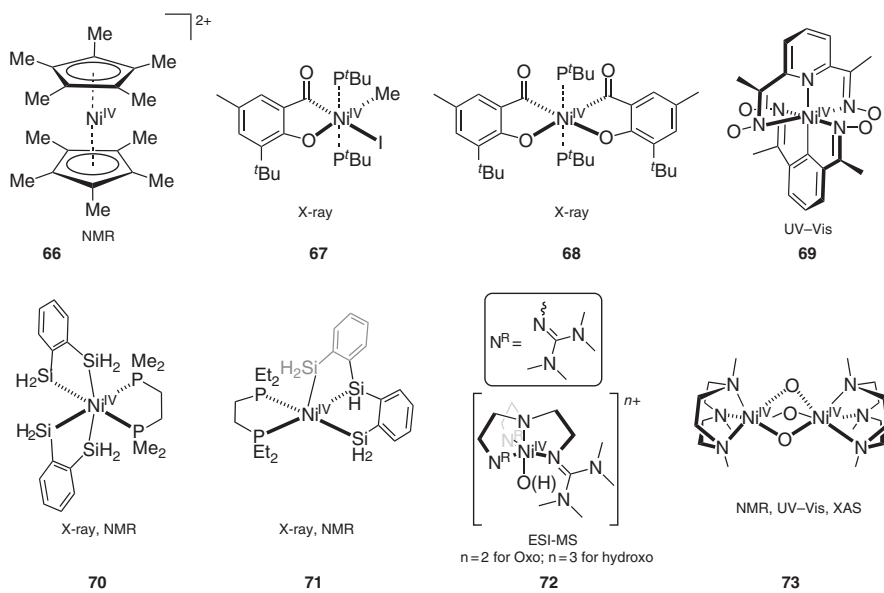


Figure 10.37 Additional isolated Ni^{IV} complexes.

coworkers isolated an octahedral Ni^{IV} complex **69** stabilized by two tridentate 2,6-diacetylpyridine dioxime ligands [58, 59]. A bis(disilyl)-Ni^{IV} complex **70** was isolated in 1999 by Tanka and coworkers [60], while in 2004 Saigo and coworkers reported a (trisilyl)Ni^{IV} complex **71** [61]. Ray and coworkers reported in 2012 a trigonal bipyramidal Ni^{IV}-oxo species **72** supported by the tetradentate ligand (tris[2-(*N*-tetramethylguanidyl)ethyl] amine) and that was observed by ESI-MS [53]. Interestingly, the first dinuclear Ni^{IV} complex **73** was recently reported by Browne and coworkers, in which the Ni^{IV} centers are stabilized by two 1,4,7-trimethyl-1,4,7-triazacyclononane ligands and bridged by three μ -oxido groups [62].

10.5 Conclusions and Outlook

This chapter provides an overview of the organometallic chemistry of isolated Ni^{III} and Ni^{IV} complexes and the proposed involvement of Ni^{III} and Ni^{IV} intermediates in various organometallic transformations. Although most C–C and C–heteroatom coupling reactions that are catalyzed by Ni are proposed to involve mostly Ni^{0/III} oxidation states, in the past decade there has been increasing evidence for the participation of Ni^{III} and Ni^{IV} intermediates in various organometallic transformations.

The first mononuclear organometallic Ni^{III} complex was observed in 1978, but it was not until 1983 when an organometallic Ni^{III} complex was actually isolated. Starting in 1995 there have been several reports proposing the involvement of Ni^{III} species during oxidatively induced C–C and C–heteroatom bond formation reactions from Ni^{III} precursors. However, it is only during the past decade that several isolated organometallic Ni^{III} complexes have been reported and their C–C and C–heteroatom bond formation reactivity studied in detail.

The first isolated organometallic Ni^{IV} complex was reported in 1982, but it was not until 2003 when the first C–C bond formation reactivity from Ni^{IV} organometallic complexes was observed. During the past five years there have been several reports showing the direct involvement of Ni^{IV} species in C–C and C–heteroatom bond formation reactions. In addition, dinuclear Ni^{III} complexes that are not stabilized by a Ni–Ni bond and their role in catalytic processes have also been reported. Most importantly, the interconversion between Ni^{III} and Ni^{IV} complexes has been demonstrated, suggesting that it is not always possible to unambiguously confirm the oxidation state responsible for the observed reactivity.

Finally, we envision that in the near future the chemistry of these less common oxidation states of Ni will lead to novel organometallic reactions that involve one- and two-electron oxidation processes. This includes higher yielding C–C and C–heteroatom bond formation reactions and a better understanding of the catalytic cycles involving high-valent Ni species. Specifically, we anticipate that Ni^{IV} complexes can be tailored to promote selective C(sp³)- and C(sp²)-heteroatom coupling reactions. A key challenge for achieving this objective will be to define a class of oxidants and supporting ligands that selectively support the Ni^{IV} oxidation state rather than a Ni^{III} oxidation state. This should enable the design of

catalytic sequences in which a Ni—C bond forming step is coupled with oxidation and C–heteroatom coupling via a Ni^{II/III/IV} catalytic cycle.

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